A STUDY OF THE REDUCTION, ALKYLATION, AND REDUCTIVE ALKYLATION OF A VOLATILE BITUMINOUS COAL

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INTRODUCTION

Reduction, alkylation, and reductive alkylation have been investigated by several different research groups to increase the solubility of coals for structural studies and to develop a greater understanding of the chemical factors essential for the conversion of the intractable coal molecules into soluble or liquid products (1,2). Several lines of evidence suggest that the higher ranking bituminous coals with 88 to 89% C(daf) are more readily converted to products that are soluble in common organic solvents than the lower ranking bituminous or subbituminous coals. The structural factors responsible for the facile reduction reactions of the higher ranking coals have not, as yet, been established. Accordingly, we have undertaken astudy of the relative effectiveness of reduction, alkylation, reductive alkylation and other reactions for the conversion of a vitrinite-rich, low volatile bituminous coal from the lower Kittanning seam in Pennsylvania--PSOC 1197--to soluble products and compared the results obtained in this work with the results obtained in previous studies of lower ranking coals.

EXPERIMENTAL PART

The coal sample was obtained from the Pennsylvania State University Sample Bank. The sample was ground to -325 mesh and then dried in vacuum at 60°C to constant weight.

Reduction.--The coal was reduced in three different ways: A) the coal (1 g) was suspended in liquid ammonia (200 ml) with 64 mmoles of potassium; B) the coal (1 g) was suspended in liquid ammonia (200 ml) with 110 mmoles of potassium; C) the coal (1 g) was suspended in liquid ammonia (200 ml) with 68 mmoles of potassium and 68 mmoles of 2-methyl-2-butanol. All the reactions were carried out at -78°C for 6 hours. Ammonium chloride was added to the reaction mixture to destroy any residual potassium and, thereby, interrupt the reaction. The ammonia was then evaporated and dilute aqueous hydrochloric acid was added to the residue. The mixture was filtered and the solid coal product was collected and dried in a vacuum oven at 60°C.

Alkylation.--The sample of PSOC-1197 was also alkylated in three different ways. Reductive butylation was carried out as described in a previous publication from this laboratory (3). About 60 mmoles of potassium and 80 mmoles of butyl iodide were used in the reaction. Non-reductive butylation was conducted using sodium amide in ammonia at -78°C as described by Ignasiak and coworkers (4). In this reaction, the coal (1 g) was treated with sodium amide (15 mmoles) for 6 hours. 1-Butyl iodide (15 mmoles) in benzene (50 ml) was then added to the reaction mixture which was stirred for 48 hours. The reaction was terminated by the addition of dilute, aqueous hydrochloric acid. The acidified coal product was collected and dried in vacuum at 60°C. The conventional alkylation reaction was carried out as described by Liotta and his coworkers (5). The coal (1 g) was stirred with 22% tetrabutylammonium hydroxide (30 ml) for 3 hours. 1-Butyl iodide (15 mmoles) in tetrahydrofuran (50 ml) was added and the suspension was stirred for 2 days. The reaction mixture was acidified by the addition of dilute hydrochloric acid. The product was then collected by filtration, washed with water, and dried in vacuum at 60°C.

Measurements.--The solubilities of the coals and the freshly prepared reaction products in pyridine and tetrahydrofuran were determined by Soxhlet extraction. Elemental analyses were obtained by the Huffmann Laboratories and by the Illinois State Geological Survey. The solid state carbon NMR spectra (CP/MAS) were measured at the National Science Foundation Regional Center at Colorado State University using a JEOL FX 60Q system. The acidities of the coals and the reaction products were determined using the procedures described by Schafer (6) and Mallya and Zingaro (7).

RESULTS AND DISCUSSION

The results obtained in this investigation of the reduction, alkylation, and reductive alkylation of a low volatile, bituminous coal with 88% C(daf) are summarized in Tables 1, 2, and 3. The original coal is only modestly soluble in tetrahydrofuran and in pyridine. However, the reduction reactions of this coal with potassium in liquid ammonia, reactions 1 and 2 in the Tables, proceed readily to yield substances that are much more soluble in the organic solvents than the original coal. The facility with which this coal is reduced is remarkable, but not unexpected in view of the results obtained by Given, Wender, and their associates in studies of the reduction of similar high ranking coals under more vigorous conditions, for example with lithium in ethylene diamine (2). In contrast, Illinois No. 6 coal is neither reduced nor rendered soluble to a significant degree by reduction in liquid ammonia (1,3).

The reduction of the Lower Kittanning coal with 110 mmoles potassium/g coal provides a much more soluble product than the reaction with 64 mmoles potassium/g coal. The reducing agent was not consumed in these reactions. The microanalytical data suggest that about 10 hydrogen atoms/100C are added to the coal in the reaction with 64 mmoles potassium/g coal and that about 12 hydrogen atoms/100C are added in the reaction with 110 mmoles potassium/g. While it is well known that the microanalytical determinations of the hydrogen content of coals and coal products are subject to relatively large errors, we have no reason to doubt the reliability of the data presented in Table 2. Thus, it seems quite pertinent that the difference in the degree of reduction of the two samples is very modest compared to the change in solubility from 25 to 78% in tetrahydrofuran and from 39 to 92% in pyridine. These two reaction products also have virtually identical acid contents, Table 3. Thus, ether cleavage reactions do not appear to be responsible for the much greater solubility of the reaction product obtained with the greater concentration of the reducing agent. The observations are compatible with the idea that additional carbon-carbon bond cleavage reactions occur when the concentration of the reducing agent is increased. Metals in ammonia both reduce and fragment hydrocarbons such as the tetraarylalkanes as illustrated in equation 1) (1,8). Accordingly, we postulate that the higher concentration of reductant leads to a greater steady state concentration of aromatic anions with the result that a somewhat greater fraction of these reactive intermediates undergo carbon-carbon bond cleavage reactions during the reaction interval to produce more soluble, lower molecular weight products. Only a few additional cleavage reactions are required to account for the observations.

$$Ar_2CHCHAr_2 \rightarrow [Ar_2CHCHAr_2]^{\dot{-}} \rightarrow Ar_2CH^- + Ar_2CH\cdot \qquad 1)$$

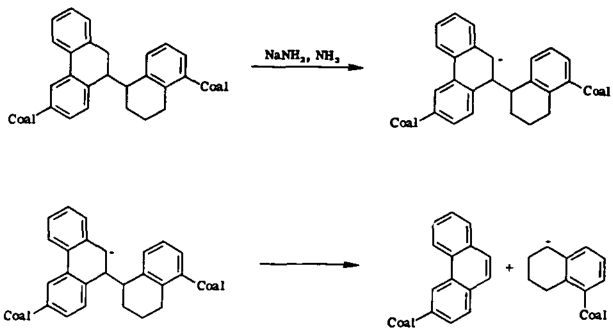
The reduction of the Lower Kittanning coal with potassium and 2-methyl-2-butanol in liquid ammonia at low temperature provides an even more soluble product, Table 1, reaction 3. As in the previous case, this reaction is ineffective for the reduction or solubilization of Illinois No. 6 coal (1). The microanalytical data imply that about 14 hydrogen atoms/100C have been incorporated into the structure of the low volatile bituminous coal. The f(A) values determined at the National Science Foundation Center at Colorado State University, for the reduction product, $f(A) = 0.69$, and the coal, $f(A) = 0.82$, imply that 21 hydrogen atoms/100C have been added to the coal. The large change in aromaticity strongly suggests that the aromatic anions and carbanions formed in the initial reduction reactions of this coal are efficiently trapped by the proton donor and converted to alkylaromatic compounds, dihydroaromatic compounds, and similar kinds of materials. The fact that a much more soluble product is formed in this reaction in which the aromatic anions of unstable compounds are rapidly protonated by the alcohol implies that reduction is as important as carbon-carbon bond cleavage in the solubilization of this coal as illustrated in equation 2)

$$[HArCH_2CH_2ArH]^- \begin{cases} \longrightarrow HArCH_2\cdot + HArCH_2^- \\ \xrightarrow{H^+} HArCH_2CH_2ArH_2 \end{cases} \qquad 2)$$

The lower Kittanning coal contains 3.3 oxygen atoms/100C. Consequently, we also investigated the role of ether cleavage reactions in its reduction reactions. The original coal contains about 0.5 meq/g of acidic hydroxyl groups; hence there is 0.6 reactive hydroxyl group per 100 carbon atoms. Within the limits of the experimental error, the acidic hydroxyl group content of the reduction products is the same as that of the original coal. To examine this issue in another way, we alkylated the product of the reduction reaction with carbon-13 labeled methyl iodide and recorded the NMR spectrum of the products. No resonance signals were observed for O-methylation derivatives between 50 and 63 ppm. Thus, there are few acidic hydroxy groups in the coal product and ether cleavage reactions do not contribute in an important way to the solubilization of this high rank coal during reduction reactions in liquid ammonia. These results are compatible with the idea that the coal contains heterocyclic ethers such as dibenzofuran. Compounds of this type are reported to undergo reduction rather than carbon-oxygen bond cleavage when treated with metals in liquid ammonia (9).

The lower Kittanning coal was alkylated in two ways. First, the reaction was carried out with a relatively mild base, tetrabutylammonium hydroxide, and 1-butyl iodide in aqueous tetrahydrofuran as described by Liotta and his coworkers (5). This reaction was ineffective for the solubilization of the coal which has less than one acidic hydroxyl group per 100 carbon atoms. In a second attempt to alkylate this coal, the reaction was carried out with sodium amide in liquid ammonia using 1-butyl iodide using a modification of the procedure developed by Ignasiak and his coworkers (4). This method provided a product that was 69% soluble in tetrahydrofuran and 83% soluble in pyridine. The result contrasts sharply with the findings obtained previously for the Illinois No. 6

coal which was not solubilized by this technique (1). The microanalytical data and the carbon NMR spectrum of the product obtained in a non-reductive alkylation with carbon-13 enriched methyl iodide are incompatible with a high degree of alkylation of the coal. These observations, therefore, imply that base-catalyzed carbon-carbon bond cleavage reactions, equation 3) are more important for the solubilization of this coal than the alkylation reactions of the carbanions formed during the reaction.



3)

Reductive alkylation of lower Kittanning coal with potassium and 1-butyl iodide provides virtually complete conversion of the material into soluble products. The exact weight gain could not be measured because it was not possible to remove the organic contaminants, for example residual 1-butyl iodide, without also dissolving the reductively butylated coal. The microanalytical data imply that more than six butyl groups/100C have been incorporated into the structure. The degree of solubilization of this coal is significantly greater than the degree of solubilization of the Illinois No. 6 coal realized in the same reaction. The carbon-13 NMR spectrum of the reductive methylation product obtained in the reaction with carbon-13 enriched methyl iodide exhibits an intense band in the C-methyl region from 15 to 40 ppm, but only very weak, almost imperceptible resonances in the O-methyl region between 55 and 65 ppm. Thus, as in the other reduction reactions of this coal, O-alkylation is an insignificant process. The resonances of the C-methyl groups added to the coal appear in three distinct regions near 22, 28, and 35 ppm, respectively. Unfortunately, the resonances are quite broad and it will be necessary to examine other C-alkylation products to assign these resonance signals with confidence.

CONCLUSION

Generally, coals are regarded as insoluble, intractable substances because of their macromolecular character, significant hydrogen bonding interactions, and the intermolecular interaction between unbonded aromatic molecules in different fragments of the structure. Solubilization can be realized when these interactions are disrupted or when the molecular weight is reduced.

Inasmuch as there are few acidic hydroxyl groups in the lower Kittanning coal, hydrogen bonding interactions do not play an important role in determining its behavior in solubilization. Thus, O-butylation of the original coal results in only a very modest increase in solubility. Moreover, no O-alkyl groups are introduced into this coal during reductive alkylation.

The carbon-oxygen and carbon-carbon bond cleavage reactions can reduce the molecular weight of coal molecules. Several lines of evidence indicate that ether cleavage reactions play an insignificant role in the reactions of the lower Kittanning coal. First, there is no increase in the content of acidic hydroxy groups after reduction. Second, there are only traces of O-alkylation products in the reduced coals. Thus, carbon-carbon bond cleavage reactions are much more probable under the conditions of these experiments. The fragmentation reactions of anion radicals such as the simple reaction illustrated in equation 1) occur during reduction and reductive alkylation. Base-catalyzed carbon-carbon bond cleavage reactions of hydrocarbons, as illustrated in equation 3) may occur in the presence of the strongly basic reagents during the non-reductive alkylation reactions. The available results indicate that reduction alone leads to significant increase in solubility and that reductive butylation using the same quantity of reducing agent yields an even more soluble product. Also, previous studies by Wachowska and her associates (10) indicate that the introduction of the large butyl and octyl groups has a large impact on the solubility of the higher rank coals. All these observations are in accord with the suggestion originally made by Wender and his associates that the introduction of hydrogen atoms into coals with significant aromatic character resulted in a disruption of the structure and a reduction of the attractive forces between non-bonded aromatic structures. The impact of the addition of hydrogen atoms is augmented, of course, by the introduction of large alkyl groups. Hence, reduction and alkylation when accompanied by the facile carbon-carbon cleavage in the highly aromatic coal structures provide quite soluble products.

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Table 1. A Summary of the Results Obtained in the Reduction, Alkylation, and Reductive Alkylation of a Low Volatile Bituminous Coal from the Lower Kittanning Seam (PSOC 1197).

	Result		
Sample Origin	Weight Gain (%)	Extractability (%,daf)[a] Tetrahydrofuran	Pyridine
Original coal	-	4	6
1. Reduction, K(64 mmoles/g), NH_3, -78°C, 6 hrs	3	25	39
2. Reduction, K(110 mmoles/g), NH_3, -78°C, 6 hrs	2	78	92
3. Reduction, K(68 mmoles/g), t-C_4H_9OH, NH_3, -78°C, 6 hrs	5	94	96
4. Alkylation, $N(C_4H_9)_4OH$, C_4H_9I (13 mmoles/g), THF, Ambient T, 48 hrs	1	16	10
5. Alkylation, $NaNH_2$, C_4H_9I (13 mmoles/g), NH_3, -78°C, 6 hrs	2	69	83
6. Reductive alkylation, K(60 mmoles/g), NH_3, 6 hrs, -78°C, C_4H_9I (80 mmoles/g), THF Ambient T, 48 hrs	-	98	93

[a]The precision realized in replicate experiments is about ± 2%.

Table 2. Microanalytical Data for the Lower Kittanning Coal (PSOC 1197) and Its Reaction Products

Sample Origin	Analytical Data (%, daf)			
	C	H	N	Ash[c]
Original coal[a]	87.4	4.8	1.4	11.3
Reduction, reaction 1[a]	84.9	5.2	1.5	10.3
Reduction, reaction 2[a]	82.9	5.1	1.6	10.3
Reduction, reaction 3[b]	86.4	5.5	1.1	10.8
Alkylation, reaction 4[a]	88.1	4.8	1.7	13.7
Alkylation, reaction 5[a]	88.9	4.8	1.8	10.3
Reductive alkylation, reaction 6[a]	82.5	8.0	1.6	5.7

[a]The analysis was performed by Dr. C. Chaven, Illinois Geological Survey.

[b]The analysis was performed by Huffmann Laboratories, Wheatridge, Colorado.

[c]The analysis was performed in this laboratory.

Table 3. Aromaticity and Acid Group Concentration in the Lower Kittanning Coal (PSOC 1197) and Its Reduction Products.

Sample	Acidity (meq/g, daf)		
	Total	Carboxylic Acid	f(A)[a]
Original coal	0.40	<0.01	0.82
Reduction, reaction 1	0.36	-[b]	
Reduction, reaction 2	0.54	-[b]	0.76
Reduction, reaction 3	0.50	<0.01	0.69

[a]The fraction of aromatic carbon content, f(A) = [(C-C(Aliphatic)/C] where C = Area of All Carbon Resonance Signals and C(Aliphatic) = Area of the Aliphatic Carbon Resonance Signal, was determined using CP/MAS NMR spectroscopy.

[b]The carboxylic acid content was not determined.